



Downwind O₃ and PM_{2.5} speciation during the wildfires in 2002 and 2010



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HIGHLIGHTS

- An increase of over 10 ppbv O₃ in both major cities and rural areas.
- O₃ enhancement coincided with that of CO and NO_x.
- Dominant carbonaceous species were OC3, pyrolysis C and EC1 originating from wood burns.
- Downwind indoor exposure depends on the penetrations into homes.

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ABSTRACT

A series of wildfires in northern Quebec, early July 2002, and in southern Quebec, late May 2010, resulted in severe air pollution downwind. Downwind exposures were investigated to estimate the impact on outdoor and indoor environments. The plumes derived from the wildfires resulted in an increase of over 10 ppbv ozone (O₃) concentrations in both major cities and rural areas, while O₃ enhancement was not observed at locations adjacent to wildfire burning areas. Temporal trend in PM_{2.5} concentration showed a peak of 105.5 µg/m³ on July 7, 2002, while on May 31, 2010 the peak was 151.1 µg/m³ in Boston downwind. PM_{2.5} speciation showed similar trends between the episodes, along with spikes in the PM_{2.5}/PM₁₀ ratio, and in the concentrations of Black Carbon, ΔC (i.e., UV absorbing compounds minus Black Carbon), Organic Carbon (OC), potassium, and chlorine. OC was the most dominant constituent of the PM_{2.5} mass in the wildfires. The dominant specific carbon fractions include OC fraction 3, pyrolysis carbon, and EC fraction 1, likely due to pyrolysis of structural components of wood. Indoor PM_{2.5} peaks at two houses corresponded well with the ambient PM_{2.5} peak, along with the elemental composition, which could indicate an impact of wildfires on indoor air pollution exposure.

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1. Introduction

Wildfires are known to be major sources of naturally-derived air pollutants on both regional and global scales. Massive smoke plumes by wildfires in tropical regions have also been found over the oceans and even the Arctic. Plumes contain trace gases including non-methane hydrocarbons (NMHCs), carbon monoxide (CO), and nitrogen oxides (NO_x), as well as large amounts of aerosols, which are important precursors to photochemical production of tropospheric ozone (O₃) (Wotawa and Trainer, 2000; McKeen

et al., 2002). O₃ levels were significantly enhanced in the plumes which could lead to impacts on the O₃ budget over a large region, with increased background O₃ levels at remote regions (Jaffe et al., 2003, 2004, 2008; Lapina et al., 2006). However, the impact of wildfires on O₃ level downwind varied significantly with the magnitude of aged plumes (i.e., distance to a receptor), the amount of biomass consumed, fuel type, burning area, and combustion conditions (Jaffe et al., 2003, 2008; Martin et al., 2006).

The particles in smoke plumes are not easily removed by gravitational settling so, along with trace gases including O₃, they can be long-range transported and lead to high risks to both human health and climate change. A number of studies have confirmed that wildfire smoke plumes can be transported over hundreds of kilometers as haze layers with elevated concentrations of trace gases which are converted to other gases or into particles in downwind

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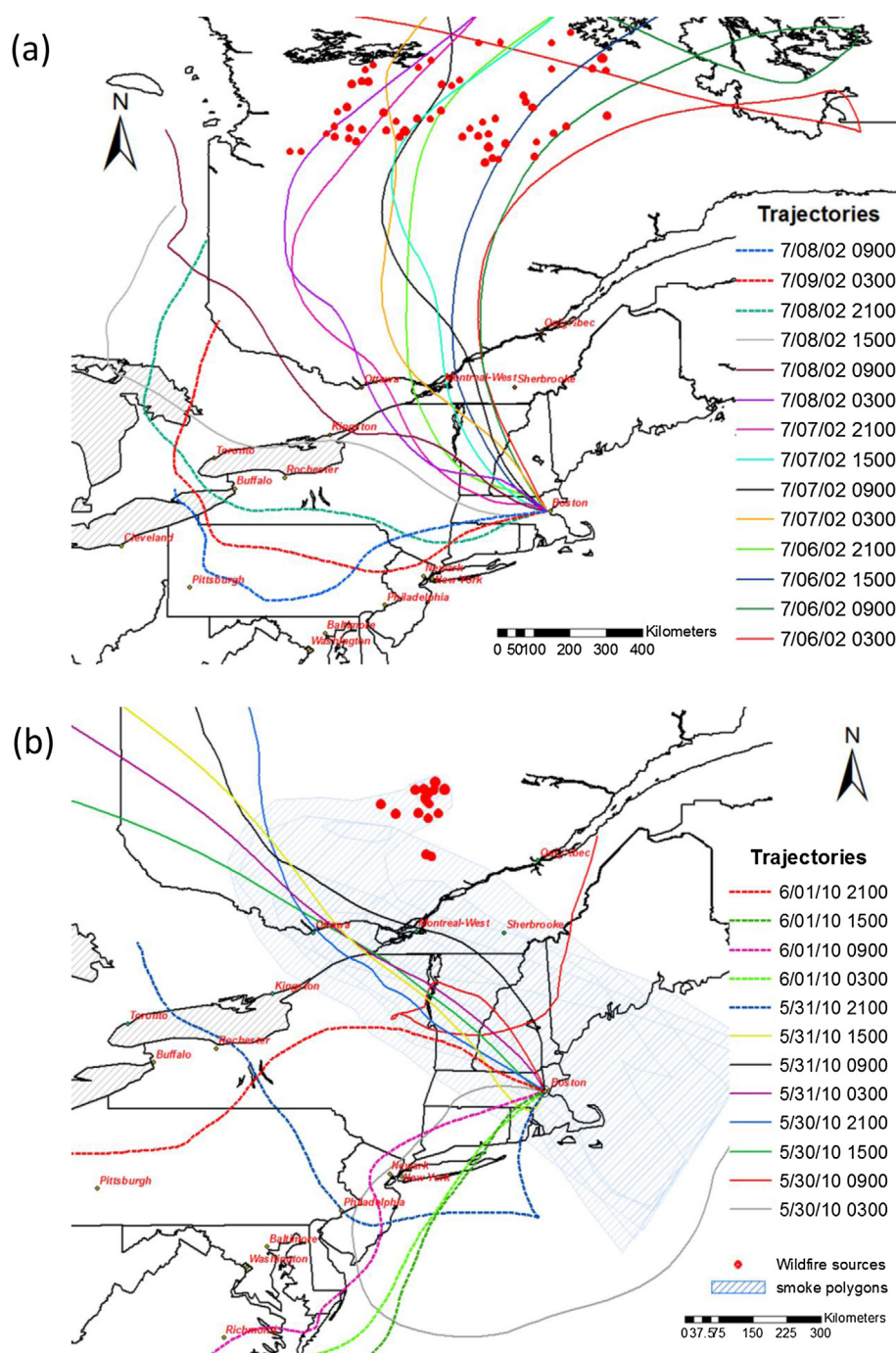


Fig. 1. Wildfire source areas, trajectories, and sampling sites: (a) wildfire sources and trajectories during the 2002 episode; (b) wildfire sources and trajectories during the 2010 episode.

areas, including Arctic areas (Wotawa and Trainer, 2000; Wofsy et al., 1994; Echalar et al., 1995; Colarco et al., 2004; Reid et al., 2005; Stohl, 2006). In Eastern Asia, in addition to natural wildfires, agricultural residual burning has caused severe air pollution downwind, including many highly populated cities (Kang et al., 2004; Hao and Liu, 1994), and also cause increasing O_3 background levels on the west coast of the U.S. (Jaffe et al., 2003).

Wildfire-derived smoke plumes contain mostly submicron particles with a single size distribution mode which condense rapidly as cooled and aged in the atmosphere, and then grow in size by condensation (Kleeman et al., 1999; Hays et al., 2002; Bein et al., 2008). Fine particles in this size range efficiently evade the

mucociliary defense system and are deposited in the peripheral airways, where they may exert toxic effects. A number of toxic or carcinogenic compounds are present in wildfire smoke plumes, including free radicals, polycyclic aromatic hydrocarbons (PAHs), and aldehydes (Leonard et al., 2007; Pryor, 1992; Schauer et al., 2001). Wegesser et al. (2009) estimated that the California wildfires events of June 2008 resulted in particles that were more toxic to the lung, especially alveolar macrophages, than equal doses of ambient air particles collected during non-wildfire events. In addition, higher concentrations of $PM_{2.5}$ and PM_{10} have been associated with increased hospital visits for respiratory problems in affected communities (Moore et al., 2006; Johnston et al., 2002).

They also reported that emergency room visits increased substantially for asthma, bronchitis with acute exacerbation and chest pain, along with modest changes in the number of hospital admissions.

In this work, we estimated temporal trends of gaseous species and PM_{2.5} speciation in plumes downwind of the Canadian wildfires in Boston, during two episodes in 2002 and 2010. Indoor and outdoor concentrations measured simultaneously are also compared to estimate air pollution exposures downwind of the plumes. In order to estimate the effect of wildfire on O₃ levels, spatial distributions of O₃ are estimated by comparing days with the wildfires and adjacent days in Northeastern U.S.

2. Methods

2.1. Wildfire episodes

During early July 2002, lighting ignited approximately 85 wildfires in the province of Quebec, Canada. Approximately 1000 km² of forest land were destroyed. The enormous smoke plume was almost 320 km wide where it entered the United States (U.S.) over the New York and Vermont state lines and impacted several major cities in the Eastern U.S., including Boston, New York City, Baltimore and Washington, D.C. The wildfires were located more than 1000 km northwest of Boston. In late May 2010, lighting also initiated more than 50 wildfires in Quebec that burned about 880 km² of forest land, at locations about 700 km northwest of Boston. Large plumes of smoke were transported and impacted the downwind areas as far away as Cape Cod in the Eastern U.S.. The locations of wildfires were obtained from the Canadian Wildland Fire Information System (CWFIS) that is a computer-based fire management information system that monitors fire danger conditions across Canada (<http://cwfis.cfs.nrcan.gc.ca/home>).

Fig. 1a and b show backward air trajectories estimated using the HYSPLIT4 model from the National Oceanic and Air Administration/Air Resources Laboratory (Draxler and Rolph, 2014). The 3-day isentropic backward air trajectories were computed at an altitude of 500 m above ground level of the Harvard Supersite (42° 20' N latitude, 71° 06' W longitude) for the episode days. The backward air trajectories on July 7, 2002 indicate that the smoke plumes originate from wildfire areas in the Northern Quebec, Canada, passed through the upper states of U.S., including New York, Vermont, and New Hampshire. The trajectories on May 31, 2010 do not coincide with the wildfire sources but passed through the smoke polygon analyzed by the NOAA-Hazard Mapping System (http://satepsanone.nesdis.noaa.gov/pub/volcano/FIRE/HMS_smoke/2010/). Contrary to smoke days, the trajectories for adjacent days (July 8, 2002 and June 1, 2010) originate from the southwest areas which include high populated cities such as New York City, Philadelphia, and Baltimore. The NASA Moderate Resolution Imaging Spectroradiometer (MODIS) satellite mapping of remote-sensing aerosol optical depth (AOD) with the high resolution of 1 km × 1 km at 14:35 eastern daylight time (EDT) on May 31, 2010 also represents intense smoke plumes derived from extended burned areas in the Southern Quebec, which covers New England in the Northeastern U. S. (Fig. S1).

2.2. Ambient and indoor measurement

Ambient particulate samples were collected at the Harvard Supersite, which is located on the library roof of Harvard Medical School near downtown Boston. Gaseous air pollutant concentration data were obtained from two Boston U.S. Environmental Protection Agency (EPA) network stations which are within 1.5 km of the Supersite. For the spatial distribution of O₃, the data were obtained from 153 U.S. EPA stations and 112 Canada National Air Pollution Surveillance (NAPS) stations, which cover the Northeastern region

of North America. At the Supersite, a Tapered Element Oscillating Microbalance (TEOM, Rupprecht & Patashnick Co. Model 1400a, Franklin, MA) was used to continuously monitor PM_{2.5} mass concentrations during the 2002 wildfire episode. During the 2010 wildfire episode, two Beta-Attenuation Mass Monitors (BAM, Met One Instruments Inc. Model 1020, Grants Pass, OR) measured hourly PM_{2.5} and PM₁₀ mass concentrations, respectively. In order to normalize the data for different instruments, the hourly PM mass data were calibrated using 24-h PM_{2.5} and PM₁₀ filter samples collected by the Harvard Impactor (HI). Particle number (PN) concentrations were monitored using a condensation particle counter (CPC, TSI Inc. Model 3022a, Shoreview, MN). Black carbon (BC) and UV-absorbing compounds (UVC) were measured using an Aethalometer (Magee Scientific Co., Model AE-21, Berkeley, CA) based on optical transmittance at two wavelengths ($\lambda = 880$ nm and $\lambda = 370$ nm) for BC and UVC, respectively. Because at the near-UV wavelength (e.g. 370 nm) certain organic compounds (e.g. PAHs) show stronger light absorbance than at the near-infra-red wavelength (e.g. 880 nm), the UVC values can be used to indicate the presence of UV-absorbing compounds (also referred to brown carbons) (Hansen, 2005). Furthermore, because the absorption enhancement by ambient particles occur concurrently at two wavelengths, the difference between UVC and BC, ΔC , may be the most useful measurement to identify wood burning particles (Allen et al., 2004). Hourly PM_{2.5} sulfate (SO₄²⁻) concentration was measured using a Sulfate Particulate Analyzer (SPA, Thermo Electron Co., Model 5020, Franklin, MA) during the 2010 episode. The SPA measurements agreed well with integrated sulfate determination by ion chromatography (IC) (Kang et al., 2010). For the 2002 episode, the 24-h integrated sulfate concentration was determined by IC (Dionex, Model DX-120).

The 24-h integrated particulate measurements were made for PM_{2.5} and PM₁₀ mass, trace elements, and carbonaceous species. PM_{2.5} Teflon filters were analyzed for trace elements by energy dispersive X-ray fluorescence spectrometer (EDXRF, PANalytical, Epsilon 5, The Netherlands) at the Harvard School of Public Health (HSPH). The EDXRF spectrometer determined the elemental compositions for 48 elements Na (sodium) to Pb (lead). A total of 49 MicroMatter XRF standard filters were used for calibration and National Institute of Standards & Technology (NIST) standard reference materials (SRM #2783) were used as a reference to validate each XRF measurement. Of the 48 elements analyzed, 20 elements were quantified, based on the limit of detection (LOD). Organic carbon (OC), elemental carbon (EC), and carbon fractions were measured using the thermal optical reflectance (TOR) method by the IMPROVE_A protocol. According to this protocol (Chow et al., 1993), stepwise-temperature fractions, including OC1, OC2, OC3, OC4, Pyrolysis C, EC1, EC2, and EC3 were reported.

During the wildfire episode in 2010, indoor measurements were conducted in the family rooms of two homes (i.e., Home SE and Home WS) which are located about 19 km from the Harvard Supersite. Study homes were typical of one or two family nonsmoking houses in New England, a Northeastern region in the U.S. The indoor measurements were done at Home SE from May 26 to June 1, 2010, and at Home WS from May 27 to June 2, 2010. Home occupants typically opened windows and doors to promote air circulation during the warmer days, and we expected that the use of air conditioners would be very limited with ambient air temperatures of 16–22 °C during the sampling periods. Indoor activities, which might generate indoor source particles, were investigated, but indoor continuous PM_{2.5} measurement (see Discussion section) indicated that such activities did not result in a significant change in indoor air quality. Indoor continuous PM_{2.5} measurements were conducted using a SidePak (Model AM510, TSI Inc. Shoreview, MN) based on a linear relation between the intensity of the scattered light

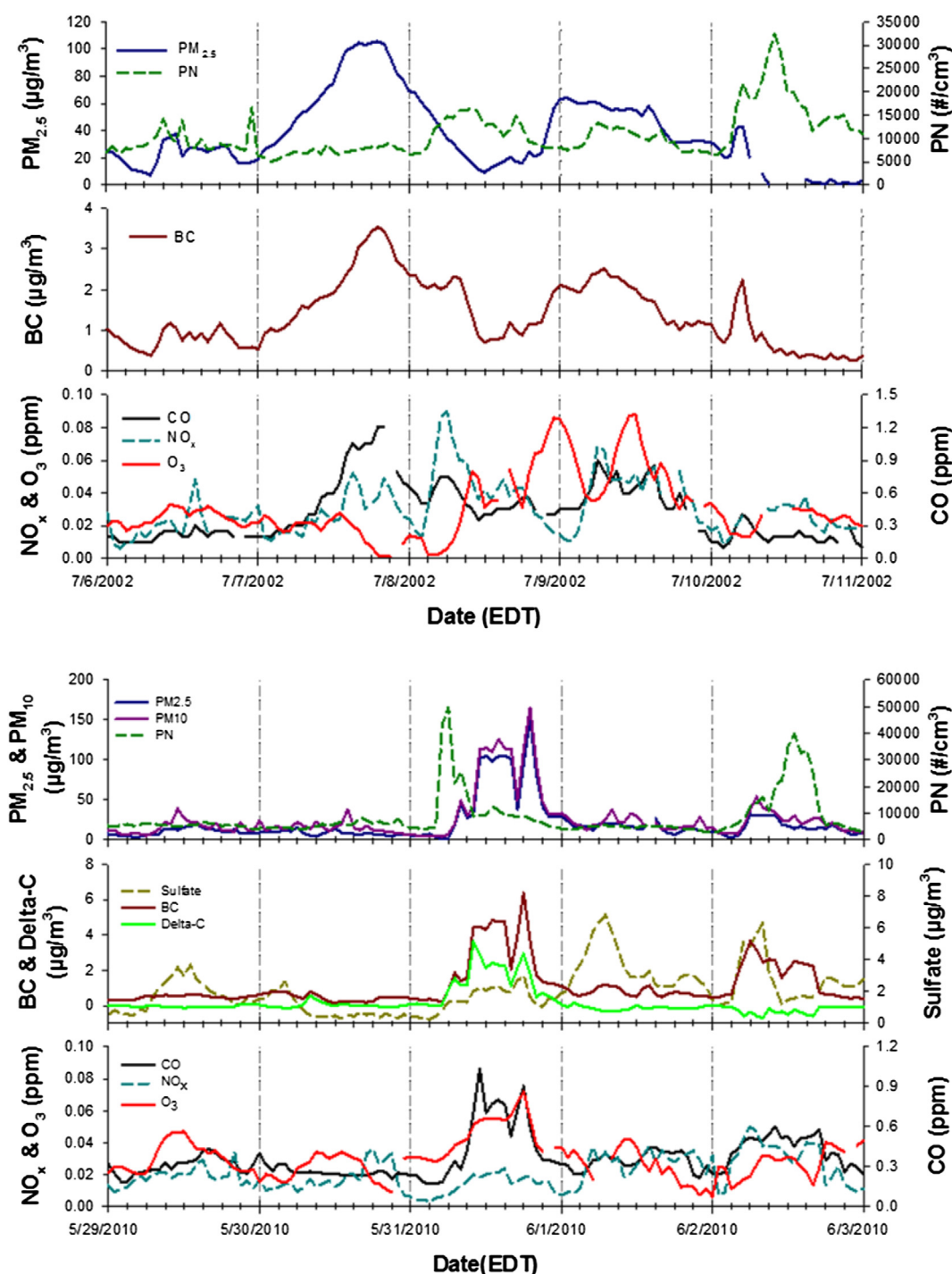


Fig. 2. Temporal trends of pollution species during the smoke episodes in 2002 and 2010; missing values were due to instrumental error.

and particle mass concentration. Simultaneous 6-day integrated $PM_{2.5}$ concentrations were used to calibrate the SidePak values. As for ambient filters, the XRF analysis was done to estimate elemental composition of the indoor particles.

3. Results and discussion

3.1. Temporal trends and chemistry of gaseous species

Air pollution data were explored for the time periods that included both a week before and a week after the smoke days (July

7, 2002 and May 31, 2010) in Boston. Temporal trends of the gaseous species during these two periods are plotted in Fig. 2. On July 7, 2002 initial spikes of CO and NO_x concentrations were observed in the early morning at 02:00 EDT. While the CO peak of 1200 ppb was observed around 19:00 EDT on the same day, coinciding with the $PM_{2.5}$ peak, the NO_x peak was observed around 06:00 EDT on July 8, due possibly to the traffic rush hour. CO and NO_x are well known as indicators of wildfire combustion (Jaffe et al., 2004; Martin et al., 2006). It has also been reported that O_3 concentrations are elevated downwind wildfires (Bein et al., 2008). For this study, background O_3 levels ranged 20–30 ppb prior to the

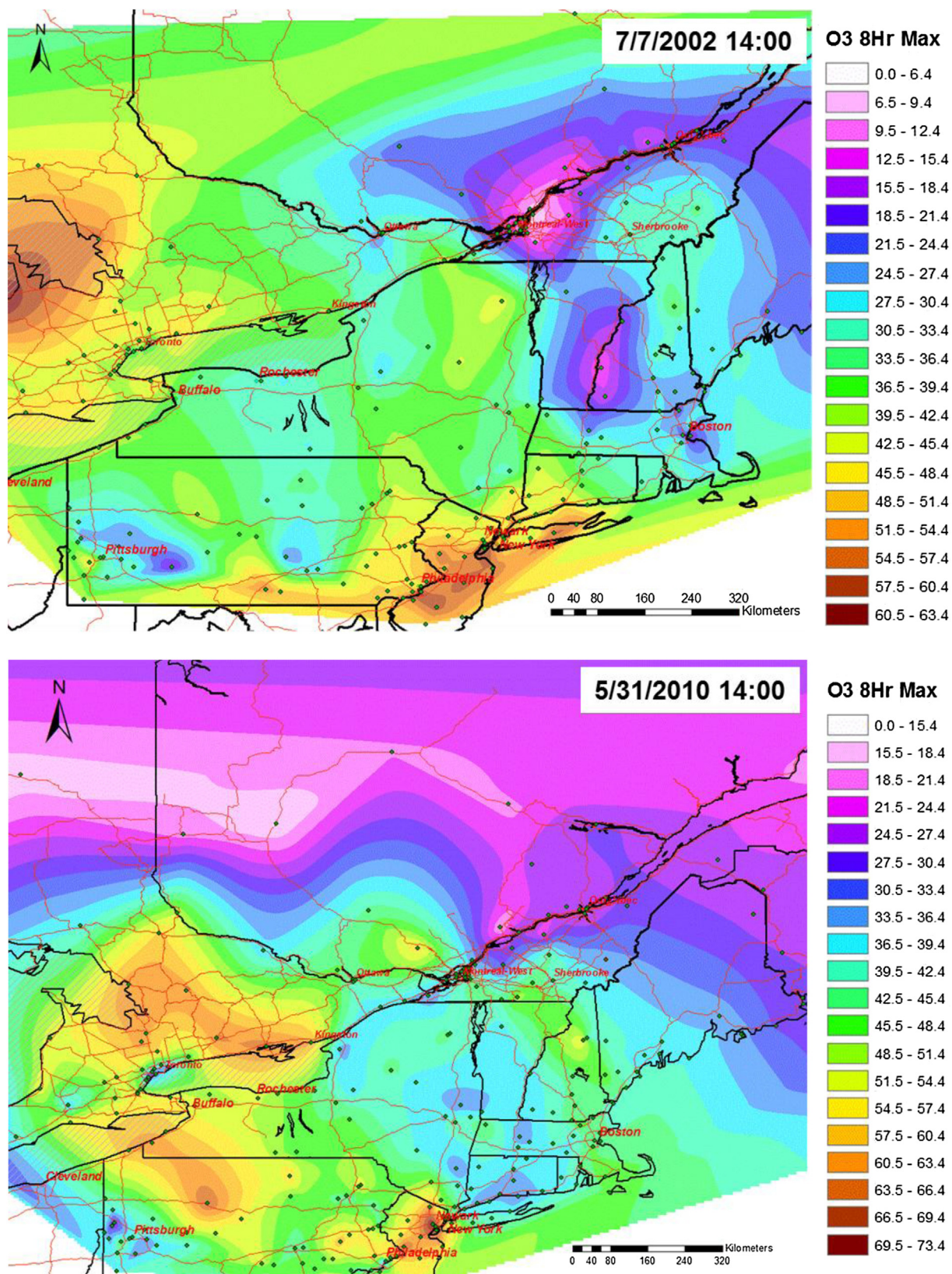


Fig. 3. Spatial maps of O₃ 8-h maximum concentrations at monitoring stations in U.S. and Canada for the smoke events.

smoke day. When the initial peak of NO_x occurred around 20:00 EDT July 7, O₃ concentration started decreasing due possibly to the NO_x titration or nighttime chemistry, and remained near zero during the remainder of the episode. One day after the maximum

wildfire impact the O₃ concentration increased significantly to 86 ppb around midnight of July 9, 2002. As of July 9 the low pressure system propagated over Boston and brought heavy rain during the night, reducing air pollution down to background levels.

As shown in Fig. 2, beginning 09:00 EDT May 31 2010, CO increased significantly and reached a peak of 1038 ppb at 11:00 EDT on the same day. In contrast to the 2002 episode, NO_x did not increase significantly, while O₃ increased and peaked at 72 ppb at 18:00 EDT on May 31, 2010, when the peaks of particulate species such as PM_{2.5}, BC, UVC, and ΔC were observed. Concentrations of CO and O₃ remained elevated until early morning on June 1 2010, when rain washed the plume out.

For the smoke day in 2002, the correlation between CO and O₃ was negative ($[O_3 \text{ ppb}] = -0.01 [CO \text{ ppb}] + 26.0, R^2 = 0.40$). In addition, the ΔO₃/ΔCO ratio, calculated from difference in the levels for adjacent and smoke days, suggests distinct behaviors of O₃ for the two plumes. For the 2002, the average ΔO₃/ΔCO ratio was −0.06, indicating a slight decrease of O₃ downwind during the episode. The decrease in O₃ level corresponding to the wildfire effect is not fully understood, but may be due to a reduction in hydroxyl radical concentrations, a loss of O₃ by reaction with organic compounds in aerosols, and nighttime chemistry (Martin et al., 2006). In contrast to the 2002 episode, for the smoke day in 2010, the correlation was significantly positive ($[O_3 \text{ ppb}] = 0.05 [CO \text{ ppb}] + 20.3, R^2 = 0.89$). For this episode, the average ΔO₃/ΔCO ratio was 0.12, suggesting a significant increase of O₃ downwind (Martin et al., 2006) found that the ΔO₃/ΔCO ratios varied significantly from −0.4 to 0.9, with an average of 0.2, during boreal wildfires. The ratios of our study are comparable with their results and the 0.1 ratio of DeBell et al. (2004) for Quebec wildfires. The variability in timing between O₃ and CO elevations for the two episodes could be explained by variation in O₃ enhancement by wildfires, which depends on several factors, such as the magnitude of aged plumes (i.e., distance to the receptor), the amount of biomass consumed, fuel type, burning area, and burning condition (Jaffe et al., 2003, 2008; Martin et al., 2006). In addition, at four sites for wildfires in early July 2002, DeBell et al. (2004) also suggested that the magnitude of O₃ enhancement varied significantly with geographic parameters which are attributed to variations in transport and surface depositional processes.

Fig. 3 shows the spatial enhancement of O₃ by the wildfires at 14:00 EDT July 7, 2002 and at 14:00 EDT May 31, 2010 when the trajectories passed clearly through the northwest, the origin of wildfire. The maps for non-smoke events, at 14:00 EDT July 10, 2002 and 14:00 EDT May 29, 2010, are also available in the supplementary (Fig. S2). The contours were plotted using ArcGIS interpolation with the O₃ 8-h maximum concentrations at monitoring stations in the U.S. and Canada. Note that the U.S. O₃ air quality standard is based on 8-h maximum concentration. For hourly concentration, the maps were almost identical to those of 8-h maximum but not shown in this paper. For both episodes, the O₃ maps indicate that significant enhancement is observed in major cities such as Philadelphia and New York City where high levels of O₃ are observed due possibly to local production during non-smoke events: 1) in 2002 for the 8-h maximum, increase up to 60 ppbv for the smoke event (for the hourly concentration, up to 100 ppbv); 2) in 2010 for the 8-h maximum, increase up to 75 ppbv (for the hourly concentration, up to 102 ppbv). In addition, the highlighted areas expand to the far north of Toronto, Canada, where O₃ levels are not high during non-smoke days: 1) in 2002 for the 8-h maximum, increase up to 47 ppbv for the smoke event (for the hourly concentration, up to 60 ppbv); 2) in 2010 for the 8-h maximum, increase up to 65 ppbv (for the hourly concentration, up to 78 ppbv). Overall, the smoke plumes result in an increase of at least 10 ppbv O₃ concentrations downwind. Specifically, significant enhancements are observed in rural areas located the north of Toronto, as well as major cities in the Northeastern U.S. The enhanced locations are similar for both episodes in 2002 and 2010. In contrast, O₃ enhancement is not observed at the locations adjacent to wildfire sources.

3.2. Temporal trends of particulate species

Temporal trends in particulate species, including PM_{2.5}, BC and PN concentrations during the wildfire in July 2002, are also plotted in Fig. 2. Beginning around 02:00 EDT on July 7 2002 the PM_{2.5} concentration increased significantly and reached a peak of 105.5 μg/m³ at 19:00 EDT on that day. Following the peak, PM_{2.5} decreased, but then increased again on July 8 to 56.4 μg/m³, possibly due to the second wildfire. BC is a good tracer of traffic emissions as well as wildfire emissions. As for the PM_{2.5} trend, BC increased significantly compared to that for non-smoke days, and then reached a peak of 3.54 μg/m³ at 19:00 EDT on July 7, coinciding with a peak of PM_{2.5} concentration, followed by the second peak on the following day between 06:00 and 07:00 EDT. However, the second peak was more likely due to traffic emissions during rush hour in Boston, as found in the previous Boston study (Kang et al., 2010). A NO_x peak was also observed between 06:00 and 07:00 EDT on July 8. In contrast to trends of PM_{2.5} and BC, PN concentration did not show a significant enhancement due to the wildfire. Fig. 2 shows hourly measurements, including PM₁₀, fine particulate sulfate, and ΔC, during late May 2010. During the 2010 episode the hourly peaks of PM_{2.5} and PM₁₀, 151.1 and 165.3 μg/m³, respectively, were observed simultaneously at 19:00 EDT on May 31. The PM_{2.5}/PM₁₀ ratio increased up to 0.91 at the peak time, due to the significant amount of submicron particles generated by wildfires and then transported downwind. An initial spike of PN concentration, about 50,000 particles/cm³, was observed at 06:00 EDT May 31, and then decreased along with PM_{2.5} and PM₁₀ concentrations. The PN concentration was also enhanced up to about 40,000 particles/cm³ at 13:00 EDT June 2 after the rain.

Hourly BC concentration increased significantly to 6.38 μg/m³ accounting for approximately 3.9% of the hourly PM_{2.5} mass concentration. The peak concentration was two times higher than that for the 2002 episode, due presumably to a closer wildfire source in 2010. In particular, ΔC, which is considered to be a good tracer in downwind effect of wildfire (Allen et al., 2004; Hansen, 2005) increased significantly during the 2010 episode. The positive ΔC values may suggest the presence of hazardous species such as PAHs during the wildfire events. For adjacent days, ΔC values were negative, which is typical for non-smoke days (Allen et al., 2004). On the other hand, the SO₄^{2−} concentration (1.9 μg/m³) averaged over the peak time (07:00 EDT on May 31 through 02:00 on June 1) did not change significantly as compared to that for the non-smoke days (2.1 μg/m³). A significant increase was observed in hourly SO₄^{2−} concentration after the rain on June 1, 2010, with a peak of SO₄^{2−} (6.8 μg/m³) accounting for 27.4% of the hourly PM_{2.5} mass at 07:00 EDT on June 1, 2010. As shown in Fig. 1, the 3-day backward air trajectories on this day changed to the southwest where big cities are located, indicating possibly that the higher SO₄^{2−} is likely to be mainly due to other sources rather than the wildfires, as found in a previous study (Zauscher et al., 2013).

3.3. Comparison of smoke and adjacent days

The combined periods of one week before and one week after the wildfire plumes arrived to Boston on July 7, 2002 and May 31, 2010 were chosen as “adjacent days”. For comparison with smoke days, July 8, 2002 and May 30, 2010, were excluded from further analysis because they represent transition patterns. The PM_{2.5} mass, sulfate, carbonaceous species and trace elements, and the PM₁₀ mass, all averaged over either the smoke or adjacent days in 2002 and 2010, are compared in Table 1 and Fig. 4.

The concentrations of PM_{2.5} and PM₁₀ averaged over either smoke or adjacent days in 2002 were approximately 30% higher than those in 2010. As compared to adjacent days, the PM_{2.5}

concentration for smoke days in 2002 and 2010 increased by factors of 3.7 and 4.7, respectively, while the increments of PM₁₀ concentrations were by factors of 3.0 and 3.3, respectively. These factors suggest that: 1) the increase of fine fraction dominates during the smoke episodes; and 2) a closer location of the wildfire source may result in higher particle concentrations. In addition, due to an influx of submicron particles in smoke plumes, the PM_{2.5}/PM₁₀ ratio was 0.99 for smoke days, while for adjacent days it was 0.81 in 2002. The PM_{2.5}/PM₁₀ ratio also increased significantly from 0.57 for adjacent days to 0.89 for smoke days in 2010. This observed ratios in this study are similar or higher compared to those reported for smoke days, 0.87, and non-smoke days, 0.67, during a Portuguese wildfire (Slezakova et al., 2006).

Fine particulate SO₄^{2−} did not change significantly during the smoke days in either year. Typically a major component of PM_{2.5}, the SO₄^{2−} concentrations accounted for 18.3 and 21.7% of the PM_{2.5} mass for adjacent days in 2002 and 2010, respectively. However, the contributions of SO₄^{2−} decreased significantly to 1.7 and 4.1% of the PM_{2.5} mass for smoke days in 2002 and 2010, respectively, indicating that sulfate was not enhanced by the wildfires. Sulfur (S) was the largest component among the elements for either smoke or adjacent days in both years even though sulfate is not likely to be emitted by the wildfires. Instead, coal combustion could be a major source of sulfate through the photochemical oxidation of SO₂ emitted from coal-fired power plants, especially in the Eastern U.S. (Kang et al., 2011).

Table 1
Compositions of ambient particles for smoke and adjacent days in 2002 and 2010.

Variables	2002 Episode		2010 Episode	
	Smoke (n = 1) ^a	Adjacent (n = 14)	Smoke (n = 1)	Adjacent (n = 13)
Hourly PM ₁₀	— ^b	—	63.2	19.1 ± 6.1 ^c
Hourly PM _{2.5}	84.3	27.7 ± 13.0	—	—
PM _{2.5}	83.1	22.3 ± 12.0	56.0	10.9 ± 4.0
PM ₁₀	84.3	27.7 ± 13.0	57.1	12.1 ± 4.3
SO ₄ ^{2−}	1.38	4.55 ± 4.08	2.32	2.74 ± 1.66
OC	42.60	8.52 ± 3.68	17.69	2.85 ± 0.55
EC	3.80	1.56 ± 0.78	2.21	0.51 ± 0.17
TC	46.40	10.08 ± 4.29	19.91	3.36 ± 0.65
BC	2.40	0.91 ± 0.39	2.49	0.70 ± 0.29
UVC	—	—	3.71	0.60 ± 0.23
ΔC ^d	—	—	1.22	0.00 ± 0.00
SOE ^e	1.05	0.77 ± 0.60	0.93	0.47 ± 0.19
Na	109.1	149.9 ± 96.0	85.1	151.9 ± 90.5
Mg	19.5	27.9 ± 25.7	12.5	14.9 ± 17.7
Al	43.9	102.3 ± 145.2	31.3	30.5 ± 16.3
Si	33.0	145.0 ± 229.0	52.3	53.1 ± 30.9
S	635.7	1616.5 ± 1407.6	774.5	954.2 ± 558.5
Cl	32.4	3.4 ± 1.8	24.8	4.0 ± 2.6
K	569.3	116.3 ± 75.4	551.2	52.5 ± 29.5
Ca	34.0	41.3 ± 32.4	45.8	29.6 ± 12.6
Ti	3.5	5.7 ± 7.7	2.0	2.3 ± 1.3
V	0.0	1.2 ± 1.0	2.8	1.3 ± 0.9
Mn	5.6	3.4 ± 2.3	9.0	2.0 ± 1.3
Fe	63.5	94.6 ± 78.1	44.9	57.1 ± 18.4
Ni	0.9	1.3 ± 0.9	0.6	1.1 ± 1.2
Cu	5.5	2.6 ± 1.6	1.2	1.5 ± 0.9
Zn	29.0	11.9 ± 4.2	36.3	5.8 ± 3.5
Se	1.2	2.4 ± 1.2	2.5	1.5 ± 1.2
Br	9.5	2.9 ± 2.5	9.7	2.3 ± 1.0
Mo	5.0	2.9 ± 1.5	2.0	1.7 ± 1.9
Ba	26.5	32.3 ± 23.2	6.2	22.1 ± 13.8
Pb	13.8	5.1 ± 3.4	0.0	3.7 ± 3.3

Unit is μg/m³ without notification and unit of elements is ng/m.³.

^a Number of samples.

^b Not available.

^c Mean ± Standard deviation.

^d ΔCarbon = UVC-BC.

^e Sum of elements excluding Sulfur.

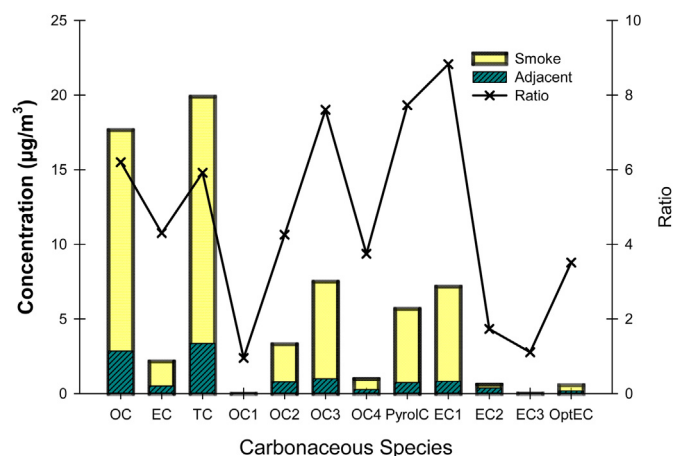


Fig. 4. Temperature-specific carbon fractions and ratios for smoke and adjacent days in 2010.

In contrast to SO₄^{2−}, both OC and EC concentrations increased substantially during the two smoke episodes. In particular, the OC concentration increased significantly during smoke days in both years, accounting for 51 and 31% of the PM_{2.5} mass (83.1 and 57.1 μg/m³ for 2002 and 2010, respectively). Accordingly, the total carbon (TC) accounted for about 56% (46.4 μg/m³) and 35% (19.9 μg/m³) of the PM_{2.5} concentrations for smoke days and 51% (10.1 μg/m³) and 32% (3.4 μg/m³) for adjacent days in 2002 and 2010, respectively. This indicates that TC, especially its OC fraction, dominates the increment in the PM_{2.5} mass during the wildfire. Temperature-specific carbon fractions are compared between smoke and adjacent days for 2010 episode in Fig. 4. Note that the carbon fractions were not available for the 2002 episode. The most significant increase was observed in OC3, pyrolysis carbon, and EC1 during the smoke days. Pyrolysis carbon and EC1, especially, are likely to be associated with wood burning. Pyrolysis carbon also accounted for 79% of the EC1 concentration during the 2010 episode. Pyrolysis of cellulose and hemicelluloses, the basic structural material constituting 65–80% of the dry weight of wood, forms stable sugar anhydrides, levoglucosan and to a lesser extent its two isomers, galactosan and mannosan (Nolte et al., 2001; Simoneit et al., 1999). These carbonaceous aerosols have been observed at high concentrations in the atmospheric aerosols associated with wood combustion. Cheng et al. (2012) also found that a considerable fraction of organic compounds from biomass samples was pyrolyzed during the carbon analysis. In addition, there were moderately increases in OC2, OC4, and Optical EC during the smoke episode, while OC1 and EC3 did not change compared to those for adjacent days. As described above, the BC concentrations increased significantly during smoke days compared to adjacent days in both years. The BC concentrations accounted for 2.9 and 4.4% of the PM_{2.5} mass for smoke days in 2002 and 2010, respectively, while the contributions were 4.5 and 6.0% for adjacent days. During the smoke days the ΔC contribution to the PM_{2.5} mass increased significantly to 2.1%, indicating the effect of wildfire smoke including hazardous species.

Elemental concentrations are also summarized by episode in Table 1. Comparing for adjacent days, well-known tracers of wood burning such as Cl and K changed significantly during the smoke days. The Cl concentrations increased significantly by factors of about 10 and 6, in 2002 and 2010, respectively, while the K concentrations increased by factors of about 5 and 11, in 2002 and 2010, respectively. In addition, Mn, Zn, and Br were moderately increased during the smoke days for both years. Furthermore,

Pearson correlation showed strong positive relationships ($r = 0.58$ – 0.87) between Cl, K, Zn, and Br for the 2002 episode while strong correlations ($r = 0.87$ – 0.96) were also observed between Cl, K, Mn, and Zn for the 2010 episode. These elements were associated with the wildfires in the previous studies (Robinson et al., 2004; Sillanpaa et al., 2005). Trace elements derived from wildfires would be primarily generated by any of the following mechanisms: 1) fine mode condensation and coagulation; 2) release of incompletely combusted plant tissues and ash, and; 3) suspension of combusted soil particles. However, process (3), would be associated with the formation of coarse particles (containing crustal elements such as Al, Si, Fe, and Ti) rather than fine particles. It is not surprising that these elements were not observed in Boston because these larger particles are not effectively transported over long distances (over 700 km) due to gravitational settling.

The contribution of K increased substantially to 33.7 and 32.3% of the total elements for smoke days in 2002 and 2010, respectively, which are comparable to the contribution of S to total $PM_{2.5}$ mass, 37.7 and 45.3%, respectively. There was also more or less enrichment of Cl, Mn, Zn, Br in addition to K compared to adjacent days. For the smoke days in 2002, the most abundant elements excluding S was K, were Na, Fe, and Al, which accounted for 53% of the total elements. For smoke days in 2010, K was the most abundant elements, followed by Na, Si, and Ca, and these elements accounted for 43% of the total elements. Robinson et al. (2004) also reported that K, accounting for 48% of total elements, was the predominate element, followed by Cl, S, and Ca in Arizona National Forest fires. The sum of elements excluding S accounted for 3.8 and 4.1% of the $PM_{2.5}$ mass for adjacent days in 2002 and 2010, respectively. On the other hand, the elemental contribution to the $PM_{2.5}$ mass decreased to 1.3 and 1.6% for smoke days in 2002 and 2010, respectively, despite the spikes of concentrations of K and Cl. This is because carbonaceous species made the main contribution to the $PM_{2.5}$ increment during the wildfires.

3.4. Impact on indoor air quality

The continuous $PM_{2.5}$ concentrations inside two homes compared to outdoor concentrations measured at the Supersite during the 2010 episode, as shown in Fig. 5. Hourly indoor $PM_{2.5}$ concentrations peaked at 19:00 EDT May 31, 2010, with 148.4 and 63.8 $\mu g/m^3$ at Home SE and Home WS, respectively. The indoor $PM_{2.5}$ peaks correspond to the outdoor peak of 151 $\mu g/m^3$ at the same time. For 6-day integrated $PM_{2.5}$ measurements, indoor $PM_{2.5}$ concentrations were 15.6 $\mu g/m^3$ and 3.6 $\mu g/m^3$ at Home SE and Home WS, respectively, while outdoor $PM_{2.5}$ concentrations averaged for each period were 18.0 and 17.6 $\mu g/m^3$, respectively. The $PM_{2.5}$ indoor/outdoor ratios were 0.87 and 0.21 at Home SE and Home WS, respectively, indicating significantly different penetration factors (Long et al., 2001). The different penetrations could be explained (at least in part) by the house location. Home WS (somewhat closure condition) is located on a high traffic highway, a favorable commute route to downtown Boston, while Home SE (open condition) is located on a peninsula into the ocean with less traffic. If elemental indoor/outdoor ratio is higher than a unity, the element can be considered to be associated with both indoor and outdoor sources.

Fig. 6 shows indoor/outdoor ratios of $PM_{2.5}$ mass and elemental concentrations during the 2010 episode. The ratios of elements above unity were found in Na, Cl, K, Ti, Zn, and Pb at Home SE. These elements are similar (or higher) to outdoor elements found during smoke days. K and Cl are considered to be tracer elements of wildfires, most likely due to the origin of outdoor. Not surprisingly, Na and Cl at Home SE located near the ocean would likely reflect

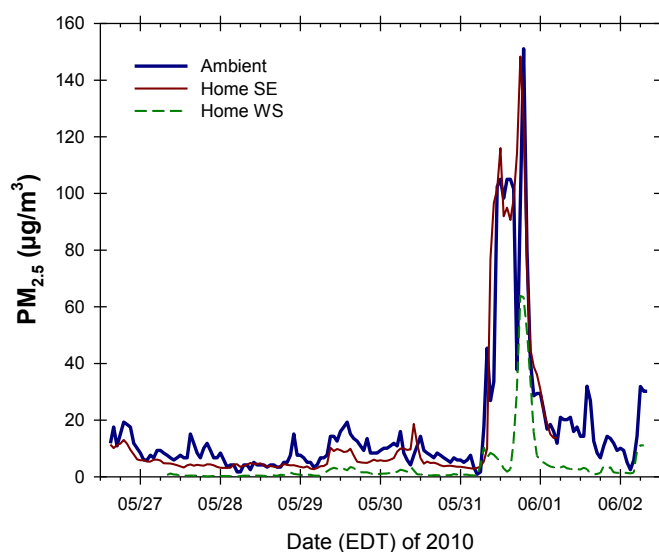


Fig. 5. Outdoor and Indoor $PM_{2.5}$ concentrations during the 2010 smoke episode.

the impact of sea salt spray. In addition, the most abundant element was S, followed by Na and K, which is similar to the outdoor $PM_{2.5}$ composition. For Home WS the indoor concentrations of all elements, excluding Ba which is a key trace element for brake wear of non-exhaust vehicle emissions (Pant and Harrison, 2013), were much lower than the corresponding outdoor concentrations. Consequently, this similarity between indoor and outdoor air quality during smoke days may indicate the effect of wildfires on indoor air quality, and the magnitude would depend on the penetration factors of home.

However, because the study only included the measurements from two homes, the sample size might be too small to draw a generalizable conclusion. Also, because the indoor measurements were conducted 19 km from the Harvard Supersite; the outdoor-to-indoor comparison might be somewhat confounded by dilution and by intense point source emissions, including those from local traffic.

4. Conclusions

A series of wildfires in northern Quebec, early July 2002, and in southern Quebec, late May 2010, resulted in severe air pollution

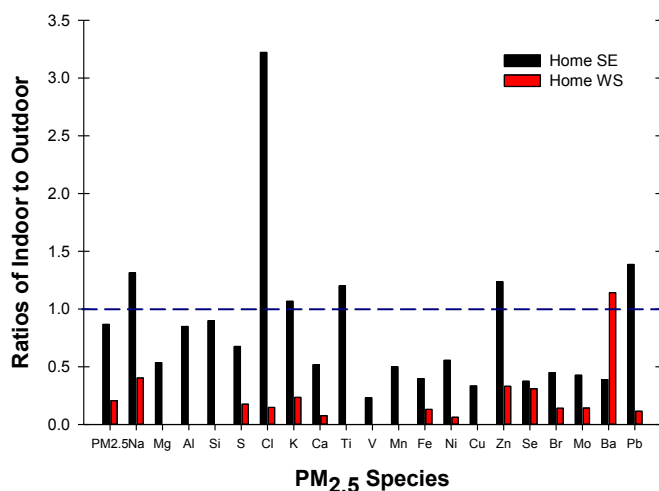


Fig. 6. Indoor/Outdoor ratios of $PM_{2.5}$ mass and elemental concentrations during the 2010 smoke episode.

downwind. Downwind exposures were investigated to estimate the impact on outdoor and indoor environments, using various techniques. Spatial maps of O₃ 8-h maximum concentrations (and hourly concentrations) at monitoring stations in the U.S. and Canada indicated that the plumes derived from the wildfires resulted in an increase of over 10 ppbv O₃ concentrations in both major cities and rural areas for the smoke events, while O₃ enhancement was not observed at locations adjacent to wildfire burning areas. Temporal trend in PM_{2.5} concentration showed a peak of 105.5 µg/m³ at 02:00 EDT on July 7, 2002, while at 19:00 EDT on May 31, 2010 the peak was 151.1 µg/m³ in Boston downwind. PM_{2.5} speciation showed similar trends between the episodes, along with spikes in the PM_{2.5}/PM₁₀ ratio, and in the concentrations of BC, ΔC, OC, K, and Cl. Of species OC was the most dominant constituent of the PM_{2.5} mass in the wildfires. The dominant specific carbon fractions included OC3, pyrolysis carbon, and EC1, likely due to pyrolysis of structural components of wood. Indoor PM_{2.5} peaks (148.4 and 63.8 µg/m³, respectively) at two houses corresponded well with the ambient PM_{2.5} peak, along with the elemental composition, which could indicate an impact of wildfires on indoor air pollution exposure. However, and the magnitude of the impact would depend on the penetrations into homes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2014.07.008>.

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